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SYNTHESIS AND THERMAL BEHAVIOR OF THE HYDROGEN PRASEODYMIUM DIPHOSPHATE ($HPrP_2O_7{\cdot}3H_2O$)

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Abstract

The preparation of a new acid lanthanide diphosphate is reported. The acid praseodymium diphosphate, obtained as a trihydrate salt, is investigated by chemical analysis, X-ray powder diffraction and IR spectroscopy. The study of the thermal behavior of $HPrP_2O_7{\cdot}3H_2O$ shows that its dehydration begins at 367 K. A scheme of its decomposition is proposed.

Keywords: chemical synthesis, diphosphate, infrared spectroscopy, thermogravimetric analysis, X-ray diffraction

Introduction

This study is a continuation of the work on acid lanthanide diphosphates. The first two identified compounds $HLaP_2O_7{\cdot}3H_2O$ and $HYbP_2O_7$ were isolated respectively from the systems $La_4(P_2O_7)_3$–$H_4P_2O_7$–H_2O and Yb_2O_3–H_3PO_4 [1–2]. They were studied by X-ray powder diffraction and thermal analysis. Later on, the synthesis of some monoprotonated lanthanide diphosphates of composition $HLnP_2O_7{\cdot}3.5H_2O$ [3] (*Ln*=La, Ce, Nd, Sm, Eu, Dy, Er, Tm, Y) and $HGdP_2O_7{\cdot}(3–4)H_2O$ [4] was reported. They were investigated by X-ray powder diffraction and IR spectroscopy. They were reported to form two isostructural groups comprising La–Sm compounds and Eu–Lu compounds. Recently, the chemical preparation and the single crystal structure of $HGdP_2O_7{\cdot}3H_2O$, crystallizing in the P-1 space group, has been reported by the authors [5]. The comparison of the powder diagrams given by Afonin [3] with that of $HGdP_2O_7{\cdot}3H_2O$ showed that the $HLnP_2O_7{\cdot}3.5H_2O$ (*Ln*=Eu–Lu) compounds are iso-

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structural with $HGdP_2O_7{\cdot}3H_2O$. So, it was concluded that the number of water molecules in these salts was 3 and not 3.5.

No investigations of acidic praseodymium diphosphate have been found. This work deals with the preparation and investigation of $HPrP_2O_7{\cdot}3H_2O$.

Experimental

The starting materials were $PrCl_3{\cdot}6H_2O$, $Na_4P_2O_7{\cdot}10H_2O$ (99%) and HNO_3 (68%).

Crystalline powder of $HPrP_2O_7{\cdot}3H_2O$ was obtained by adding 10 ml of $PrCl_3{\cdot}6H_2O$ aqueous solution ($5{\cdot}10^{-2}$ M) to 20 ml of sodium diphosphate solution (10^{-1} M), with stirring. A gelatinous precipitate appears. The latter is dissolved by adding 0.7 ml of HNO_3. The precipitate, deposed after 10 min of stirring, is filtered off on a glass filter, washed with distilled water, and dried at room temperature.

The prepared compound was analyzed for praseodymium and phosphorus photometrically using a Perkin Elmer (Lambda 11) UV visible spectrophotometer. The phosphorus was determined as a phosphovanadomolybdic complex which absorbed at 460 nm after the diphosphate had been hydrolyzed to orthophosphate in an acidic solution. Whereas the praseodymium was analyzed as a trivalent cation which absorbed in the wavelength area 575–612 nm. Linear calibration curves were used.

X-ray powder diffraction studies were carried out on a Philips PW 1710 diffractometer using CuK_α radiation. The IR spectra were recorded in the 4000–400 cm^{-1} range, on a Perkin Elmer FTIR 1000 spectrophotometer. The powder was finely ground and pressed into KBr pellets.

The thermal analysis curves were recorded in the range 20–1000°C, in an air atmosphere, on a Seiko SCC/5200 TG/DTA 320 U instrument, with a rate of 5° min^{-1}. The sample mass used was 35 mg.

Results and discussion

The acid praseodymium diphosphate is obtained as a fine green crystalline powder, practically insoluble in water but soluble in acidic solution. The chemical analysis indicates that this compound has a molar ratio $Pr^{3+}/P_2O_7^{4-}=1$. The phosphate and praseodymium contents in the elaborated salt are given in Table 1.

Table 1 Chemical analysis of acid praseodymium diphosphate

	Pr^{3+}	$P_2O_7^{4-}$	H_2O
Observed/mass%	36.43	46.60	–
Calculated/mass%	38.09	47.04	14.60

Attempts to prepare crystals for single crystal X-ray structural analysis have been unsuccessful.

The X-ray powder diffraction pattern for the hydrogen praseodymium diphosphate, given in Fig. 1a contains a series of sharp reflections.

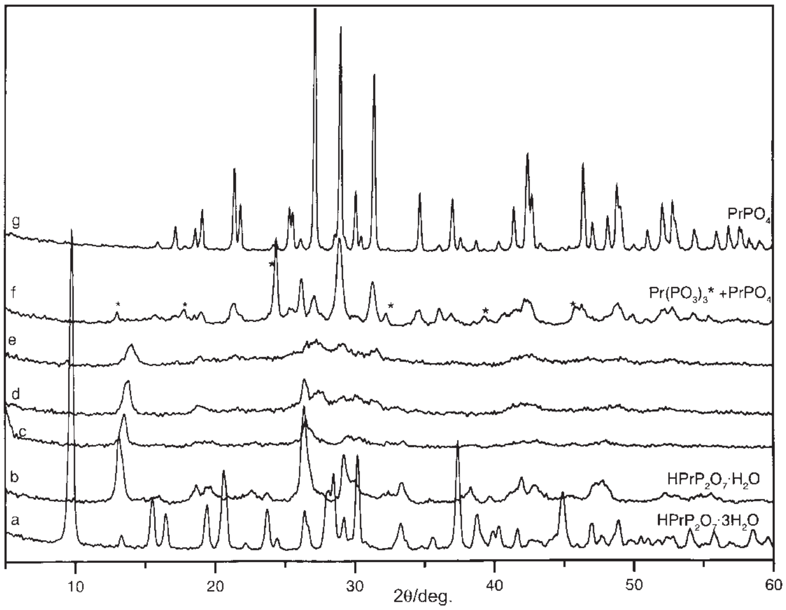

Fig. 1 X-ray patterns of $HPrP_2O_7{\cdot}3H_2O$ at different temperatures. a – dried at room temperature; b – calcined at 413 K ; c – calcined at 453 K; d – calcined at 513 K; e – calcined at 743 K; f – calcined at 953 K; g – calcined at 1373 K

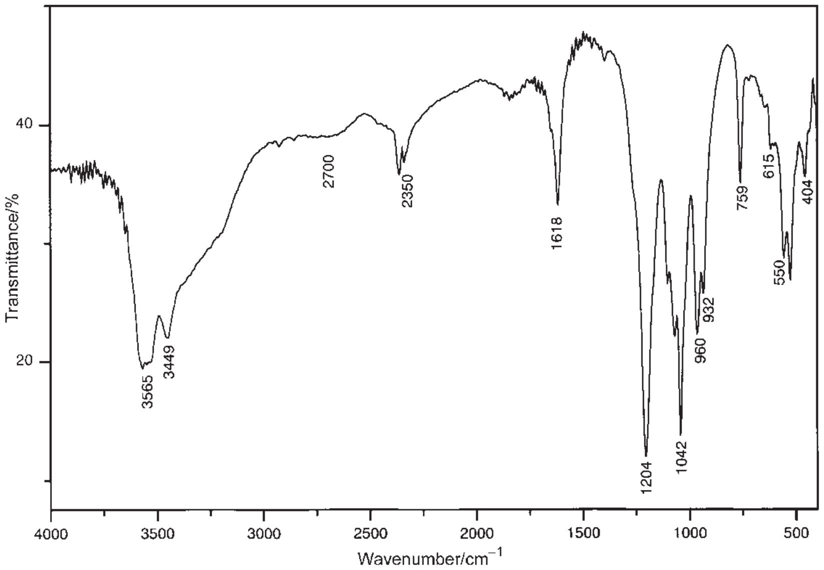

Fig. 2 IR spectrum of $HPrP_2O_7{\cdot}3H_2O$ dried at room temperature

It can be noted that these data agree with those given for $HLnP_2O_7$·$3.5H_2O$ (*Ln*=La–Sm) [3], but they don't fit the data of the gadolinium compound [5]. This makes us suppose the existence of, at least, two isostructural groups of the $HLnP_2O_7$·$3H_2O$ phosphates.

Figure 2 presents the IR spectrum of the acid praseodymium diphosphate. The characteristic bands of crystallization water can be observed at 3565, 3449 and 1618 cm^{-1}. The weak, broad absorption bands at about 2700 and 2350 cm^{-1} are characteristics of the acid diphosphates [6]. They are assigned to P–O–H stretching. The strong absorption bands observed in the 1200–1040 cm^{-1} region can be attributed to the O–P–O stretching vibrations. Whereas the split components noted at 960 and 932 and the band observed at 759 cm^{-1} are assigned respectively to the asymmetric and symmetric P–O–P stretching vibrations. These bands are characteristics of the P_2O_7 group [7]. The deformation vibrations of the P_2O_7 group appear as medium intensity bands in the 615–380 cm^{-1} range.

Figure 3 presents a curve of the acid praseodymium diphosphate on which three endothermic effects (394, 443 and 480 K) and one exothermic effect (935 K) are observed.

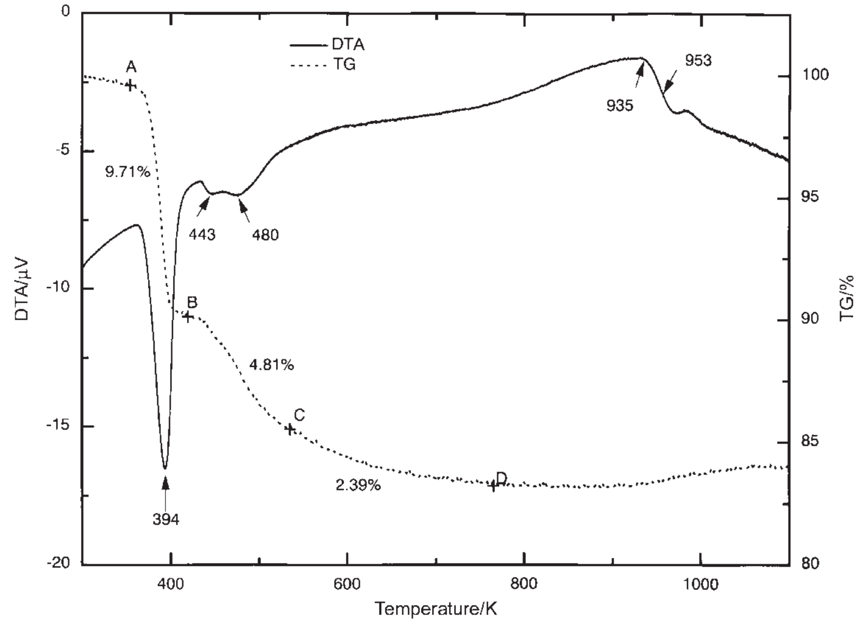

Fig. 3 DTA and TG curves of $HPrP_2O_7$·$3H_2O$

When heated to a temperature of 367–418 K (A–B), the salt loses 9.71% of its mass, which is in good agreement with the theoretical loss of 2 moles of H_2O from the trihydrate salt (9.75%). The mass loss occurring between 418–533 K (B–C) is 4.81%. It corresponds to the removal of one water mole. At 533–763 K (C–D), a half water mole is lost (2.39%). The total mass loss is then 16.91% ($3.5H_2O$).

In order to know the exact number of crystallization water moles in the elaborated product and to see the effect of its removal, heat treatment was carried out.

The elaborated product is heated in the DTA unit until a peak is obtained. When this happens, heating is stopped. The sample is cooled down to room temperature then subjected to X-ray and IR spectroscopic analysis. Heating is then, resumed with a new sample of the same compound, and treatment, as described above, was performed for each effect found in the DTA curve.

The results of the heat treatment are illustrated in Figs 1 and 4.

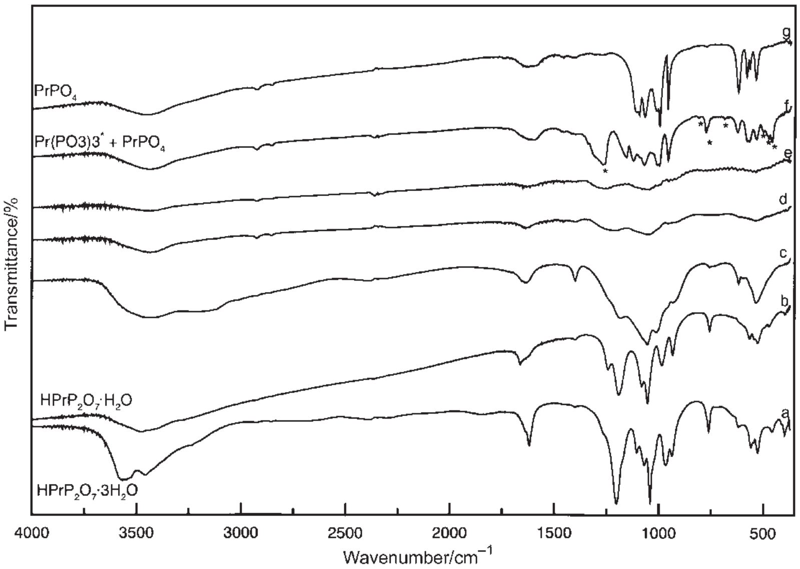

Fig. 4 IR spectra of $HPrP_2O_7 \cdot 3H_2O$ at different temperatures. a – dried at room temperature; b – calcined at 413 K; c – calcined at 453 K; d – calcined at 513 K; e – calcined at 743 K; f – calcined at 953 K; g – calcined at 1373 K

X-ray powder diffraction patterns of the product after heating at 413 K (Fig. 1b) show the formation of a crystalline compound by partial dehydration of the acid praseodymium diphosphate. The corresponding IR spectrum (Fig. 4b) does not present a great change compared to the one of the initial product.

Poorly crystallized phases are formed when the product is heated at 453, 513 and 743 K (Figs 1c–1e). Broadened bands appear on the corresponding IR spectra (Figs 4c–4e).

The X-ray pattern of the product after heating at 953 K (Fig. 1f), shows the formation of $Pr(PO_3)_3$ and $PrPO_4$ [8–9]. Only $PrPO_4$ lines were observed when the title compound is heated at 1373 K for 2 h (Fig. 1g). These results are confirmed by the IR spectroscopy. $PrPO_4$ bands can be noted in both IR spectra shown in figures 4f and 4g. Those of $Pr(PO_3)_3$ [10] are present only in the IR spectrum of the product heated at 953 K (Fig. 4f).

Therefore, we believe that the exo-effect at 935 K corresponds to the crystallization of the products resulting from the decomposition of the acid praseodymium diphosphate taking place below 763 K. This suggests that the loss of mass between 367 and 763 K can be attributed to the reaction:

$$2HPrP_2O_7{\cdot}xH_2O \rightarrow Pr(PO_3)_3+PrPO_4+(2x+1)H_2O$$

Taking into account the results of the chemical analysis, the IR spectroscopy, and the thermogravimetric analysis, the formula assigned to the synthesized salt is $HPrP_2O_7{\cdot}3H_2O$.

The study of its thermal behaviour shows that its decomposition begins at 367 K. The observed transformations can be represented schematically by the following steps.

$$HPrP_2O_7{\cdot}3H_2O \rightarrow HPrP_2O_7{\cdot}H_2O+2H_2O \qquad 367\text{–}411\ \text{K}$$

$$HPrP_2O_7{\cdot}H_2O \rightarrow \text{amorphous phase}+3/2H_2O \qquad 428\text{–}763\ \text{K}$$

$$\text{amorphous phase} \rightarrow PrPO_4+Pr(PO_3)_3 \qquad 935\ \text{K}$$

$$Pr(PO_3)_3 \rightarrow PrPO_4+P_2O_5 \qquad 1373\ \text{K}$$

Conclusions

The acid praseodymium diphosphate was synthesized and characterized by chemical analysis, X-ray powder diffraction, IR spectroscopy and thermal analysis. The study of its thermal behavior allowed us to propose a scheme of its decomposition.

The results obtained are in good agreement with the formula $HPrP_2O_7{\cdot}3H_2O$ attributed to the synthesized salt.

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